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GAS CHROMATOGRAPHIC BEHAVIOUR OF C₁-C₃ ALCOHOLS ON CARBOWAX 400*

C. BIGHLI, A. BETTI, F. DONDI AND R. FRANCESCONI**

Department of Chemistry, University of Ferrara (Italy)

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SUMMARY

The gas chromatographic behaviour of C₁-C₃ alcohols and chloroform on Carbowax 400 was studied in the range 58-88°. The specific retention volumes were determined, and the deviations from the expected order of elution were investigated by calculating the activity coefficients and the thermodynamic excess functions. The FLORY-HUGGINS theory was used to evaluate the statistical contribution made by the mixing of molecules of different sizes, and the results were interpreted on the basis of the theory of associated ideal solutions. The difference between the order of elution of alcohols and the order of their boiling points was found to be due to differences in their molecular volumes. On the other hand, the nature of the association between the alcohols and Carbowax 400 is not very different from that of the associated species in the pure alcohol samples. The relative volatilities may therefore be predicted from the FLORY-HUGGINS theory.

INTRODUCTION

Many authors have shown that it is possible to interpret gas chromatographic behaviour on a thermodynamic basis. In most cases, the systems treated involved weak interactions¹⁻³. The present article deals with the elution of substances forming hydrogen bonds, with special reference to primary, secondary, and tertiary C₁-C₃ alcohols. On Carbowax 400, these are eluted in an order different from that predicted from their boiling points, which calls for a thermodynamic explanation.

The activity coefficients will be calculated, and the thermodynamic excess functions determined. The contribution made by the mixing of molecules of different sizes to the deviation from ideal behaviour will be evaluated by the FLORY-HUGGINS theory^{4,5}, and the thermodynamic behaviour will be interpreted with the aid of the theory of "associated ideal solutions"⁶. For the sake of comparison, the method will be applied also to chloroform on Carbowax 400.

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** Department of Chemistry, University of Bologna, Italy.

EXPERIMENTAL

The measurements were done with a Fractorap GV 200 gas chromatograph (from Carlo Erba, Milano). The carrier gas was helium, so as to minimise the interaction with the solute. The samples, listed in Table I, were gas chromatographically pure products (from Fluka AG, Switzerland). The stationary phase was Carbowax 400 (polyethylene glycol = Cw 400) and the support was 60-80 mesh silanized Chromosorb P, both being products for GLC (from Carlo Erba, Milano). The operating conditions were the same as described previously⁷.

TABLE I

SPECIFIC RETENTION VOLUMES (V_g) OF ALCOHOLS ON CARBOWAX 400

Alcohols	Temperature (°C)				
	88	78	68	58	b.p.
Methanol	58.7	83.5	117.4	170.4	64.6
Ethanol	73.0	105.8	155.1	228	78.3
1-Propanol	133.9	200	300	459	97.2
2-Propanol	67.6	99.1	145.2	222	82.3
1-Butanol	252	389	610	—	117.8
2-Butanol	119.2	178.2	269	—	99.5
2-Methyl-2-propanol	56.5	82.3	120.4	—	82.5
2-Methyl-2-butanol	108.8	162.3	246	—	102.3
Chloroform	73.5	104.9	—	223	61.2

The values of the specific retention volume V_g at 58, 68, 78 and 88° are given in Table I. The activity coefficients γ (Table II) were calculated from the expression:

$$\gamma = \frac{1.7 \times 10^7}{V_g p^\circ M_L} \quad (1)$$

where M_L is the molecular weight of the stationary phase⁷, and p° is the vapour pressure of the solute at the temperature of the measurement. The values of p° were found from equations reported in the literature⁸⁻¹⁵. Since the vapour pressure was

TABLE II

ACTIVITY COEFFICIENTS γ ON CARBOWAX 400

Alcohols	Temperature (°C)			
	88	78	68	58
Methanol	0.39	0.40	0.42	0.43
Ethanol	0.52	0.52	0.54	0.57
1-Propanol	0.59	0.59	0.62	0.66
2-Propanol	0.65	0.66	0.69	0.71
1-Butanol	0.71	0.72	0.75	—
2-Butanol	0.72	0.73	0.77	—
2-Methyl-2-propanol	0.78	0.79	0.83	—
2-Methyl-2-butanol	0.85	0.86	0.90	—
Chloroform	0.35	0.32	—	0.28

TABLE III

	$\Delta\mu^E$ kcal/mole				ΔH^E kcal/ mole	ΔS^E e.u.
	88°C	78°C	68°C	58°C		
Methanol	-0.67	-0.64	-0.60	-0.55	0.6	3.5
Ethanol	-0.47	-0.45	-0.42	-0.37	0.7	3.2
1-Propanol	-0.38	-0.36	-0.33	-0.28	0.8	3.3
2-Propanol	-0.31	-0.29	-0.26	-0.22	0.7	2.8
1-Butanol	-0.25	-0.23	-0.19	—	0.8	2.9
2-Butanol	-0.24	-0.22	-0.18	—	0.8	2.9
2-Methyl-2-propanol	-0.18	-0.16	-0.13	—	0.8	2.6
2-Methyl-2-butanol	-0.12	-0.10	-0.07	—	0.7	2.1
Chloroform	-0.75	-0.79	—	-0.83	-1.8	-2.9

used instead of the fugacity, γ expresses the deviation from Raoult's law as the deviation from ideal in the solution and the gaseous phase¹⁶.

The excess partial molar free energy $\Delta\mu^E$, the enthalpy ΔH^E , and the entropy ΔS^E (cf. Table III) were obtained from:

$$RT \ln \gamma = \Delta\mu^E \quad (2)$$

$$\Delta\mu^E = \Delta H^E - T \Delta S^E \quad (3)$$

The accuracy of the thermodynamic excess functions is limited by the considerations discussed elsewhere^{17,18}. The uncertainty of M_L introduces a systematical error in the values of γ , $\Delta\mu^E$, and ΔS^E found from eqns. 1-3, but it is still possible to compare the values for individual compounds.

The statistical contribution, γ_m , made by the mixing of molecules of different sizes was then calculated in accordance with the FLORY-HUGGINS theory by means of the relationship:

$$\gamma_m = 1/m \exp(1 - 1/m) \quad (4)$$

where m is the ratio between the molecular volume of the solvent and the solute. It

TABLE IV

	γ_m	ΔS_m e.u.	$\Delta\mu_{corr.}$ kcal/ mole 78° C	$\Delta S_{corr.}$ e.u.
Methanol	0.272	2.6	0.27	0.9
Ethanol	0.372	2.0	0.25	1.2
1-Propanol	0.456	1.6	0.20	1.7
2-Propanol	0.465	1.5	0.24	1.7
1-Butanol	0.533	1.2	0.19	1.7
2-Butanol	0.534	1.2	0.20	1.7
2-Methyl-2-propanol	0.545	1.2	0.26	1.4
2-Methyl-2-butanol	0.605	1.0	0.25	1.1
Chloroform	0.482	1.4	-0.30	-4.3

was considered permissible here to use molecular volumes deduced from the density¹⁹ at 25°. The fact that the samples were not eluted at this temperature does not affect the following discussion.

The values of $\Delta S_{\text{corr.}}$ and $\Delta\mu_{\text{corr.}}$ (Table IV) were obtained from:

$$\Delta S_{\text{corr.}} = \Delta S^{\text{E}} - \Delta S_m \quad (5)$$

$$\Delta\mu_{\text{corr.}} = \Delta\mu^{\text{E}} + T \Delta S_m \quad (6)$$

where

$$\Delta S_m = -4.57 \log \gamma_m \text{ (e.u.)} \quad (7)$$

The $\Delta S_{\text{corr.}}$ function is similar in form to the Guggenheim-Miller interaction term χ (ref. 1). Since the Guggenheim-Miller theory more properly relates to solutions in which weak interactions prevail¹, the term $\Delta S_{\text{corr.}}$ will be discussed here according to the theory of "associated ideal solutions", which particularly accounts for specific and directional interactions such as hydrogen bonding⁶.

RESULTS AND DISCUSSION

The retention volumes of the samples, listed in Table I, show that the order of elution of the alcohols is different from that predicted on the basis of their boiling points, also given in Table I.

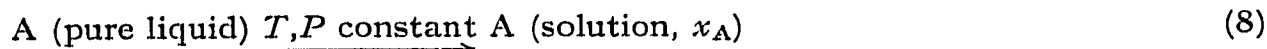
The following emerges from the data in Tables II and III, which show the activity coefficients and the thermodynamic excess functions of the samples:

(1) The activity coefficients are smaller than unity for all the four temperatures ($\Delta\mu^{\text{E}} < 0$);

(2) At a given temperature, γ distinctly increases with the chain length. For a given number of carbon atoms, γ increases (though to a smaller extent) as $1^{\text{v}} < 2^{\text{v}} < 3^{\text{v}}$ alcohol. ($\Delta\mu^{\text{E}}$ increases in the same direction);

(3) The activity coefficient decreases as the temperature is raised ($\Delta H^{\text{E}} > 0$).

It should be recalled that the function $\Delta\mu^{\text{E}}$ expresses the variation in free energy of mixing of a component of a non-ideal system in excess of that of an ideal system²⁰. This is related to the transfer of one mole of pure substance A to a solution, with a mole fraction x_A :



In particular, if ΔG_A is the variation in the partial molar free energy of substance A, it follows that:

$$\Delta\mu^{\text{E}} = \Delta G_A - RT \ln x_A \quad (9)$$

The increase in the values of $\Delta\mu^{\text{E}}$ with an increase in the carbon chain length therefore indicates that this process (eqn. 8) becomes less and less favoured. However, it is not possible to assign absolute values to $\Delta\mu^{\text{E}}$, owing to the uncertainty of the molecular weight of the stationary phase (≈ 400).

To clarify the differences in the behaviour of the alcohols, it would be advantageous to free the values of $\Delta\mu^E$ and ΔS^E from the contributions that come from the difference between the molecular volume of the solvent and that of the solute. Like others^{17,18}, we did this by determining γ_m . The values of $\Delta\mu_{\text{corr.}}$ and $\Delta S_{\text{corr.}}$, calculated from eqns. 5 and 6 (*cf.* Table IV), describe the process represented by eqn. 8, except for the contribution due to difference in volume. The values of $\Delta\mu_{\text{corr.}}$ refer to 78°, but the results for other temperatures are similar.

This correction is of considerable interest because the $\Delta\mu_{\text{corr.}}$ and $\Delta S_{\text{corr.}}$ values are less affected by the uncertainty of the molecular weight attributed to Carbowax 400. In fact, a twofold variation in the molecular weight causes less than 10% variation in the corrected activity coefficient $\gamma_{\text{corr.}} = \exp(\Delta\mu_{\text{corr.}}/RT)$, so that the following discussion is valid.

Since the solutes are pure liquids (alcohols) and mixtures (Carbowax + alcohols), it seems reasonable to describe the liquid phase by the "associated solutions" model with the simplification proposed by PRIGOGINE AND DEFAY⁶. The present system contains bonds whose energy is higher than the mean energy of thermal motion and the energies normally featuring in other models of non-ideal solutions, such as regular and athermal solutions.

According to this model, the initial state in the dissolution (eqn. 8) can be described as a mixture of agglomerates formed by alcohol molecules and having various configurations and degrees of polymerization. The final state in the process is considerably more complex. In view of the high dilution characteristic of the GLC system, however, it may be assumed that these agglomerates do not predominate over those formed between monomeric alcohols and Carbowax 400 via the ether linkages of the latter. In the case of alcohols, therefore, the mixing can be considered simply as a process in which the hydrogen bonds between alcohols are ruptured and alcohol-Carbowax bonds are formed subsequently. $\Delta\mu_{\text{corr.}}$, $\Delta S_{\text{corr.}}$ and ΔH^E are a measure of this process. Table IV shows that $\Delta\mu_{\text{corr.}}$ is positive and not very different for the various alcohols. The following emerges from these results:

(1) The differences in the values of $\Delta\mu^E$ for individual alcohols are mainly due to differences in the molecular volumes.

(2) In view of the low value of $\Delta\mu_{\text{corr.}}$, the hydrogen bonds between the alcohol molecules in the pure liquid are more stable than those formed between alcohols and Carbowax 400, but the difference is not particularly great.

Since the correction gives rise to a general levelling of the values of excess partial molar free energy, no distinct differences can be seen between the members of the homologous series and between the isomers. In other systems, however, differences in the hydrogen bonding strength were observed^{21,22}.

The conclusions drawn from $\Delta\mu_{\text{corr.}}$ are confirmed by the positive values of ΔH^E and $\Delta S_{\text{corr.}}$. This indicates that the process (eqn. 8) is endothermic and is accompanied by an increase in the number of degrees of freedom, in agreement with the weakening of the hydrogen bonds during the change from the pure liquid to the solution²³.

The values of these three excess functions for the alcohols on Carbowax 400 agree with those obtained in other solvents^{24,25} such as carbon tetrachloride, benzene, methylene chloride and chloroform (see Table V). It is evident from Table V that ΔH^E decreases with the increase of the possibility of interaction with the solvent.

TABLE V

Solvent	$\Delta\mu^E$ kcal/mole	ΔH^E kcal/mole	ΔS^E e.u.
Carbon tetrachloride (35-60°)	2.0-2.7	4-7	7-9
Benzene	~1.8	~4	~8
Methylene chloride	~1.5	~3.5	~6
Chloroform	~1.4	~2.5	~3.5
Carbowax 400 (58°)*	~0.2	~1	1-2

* The values of entropy and excess partial free energy are corrected for the effect of volume.

This can be explained by assuming that the increasing interaction with the solvent compensates more and more for the endothermic effect of the rupture of the quasi-crystalline structure of the alcohol. ΔS^E follows a parallel course, in accordance with the directional nature of the hydrogen bonds and the greater degree of order introduced by this into the solution.

The investigation was extended to the chloroform-Carbowax 400 system in order to test the interpretation based mainly on the sign of the excess functions. The theory of associated ideal solutions predicts a negative sign for $\Delta\mu_{\text{corr.}}$, ΔH^E , and $\Delta S_{\text{corr.}}$ in this case. The final state in the process (eqn. 8) is similar to that in the case of the alcohols. By contrast, the initial state is different, because the solute (chloroform) is not associated in the pure liquid state. In this case, the process is strongly exothermic, in agreement with the fact that a new bond is formed ($\Delta H^E < 0$). The sign of ΔS^E and, *a fortiori*, of $\Delta S_{\text{corr.}}$ is negative, since bond formation means a decrease in the number of degrees of freedom²³.

It appears from these considerations that the gas chromatographic behaviour of alcohols on Carbowax 400 can be predicted from the vapour pressures and the activity coefficients γ_m obtained from eqn. 4.

In this connection we calculated the volatility of the alcohols (with respect to that of ethanol), using the expression:

$$a_{\text{calc.}} = p^\circ \cdot \gamma_m / p_E^\circ \cdot \gamma_{m,E}$$

where p° and p_E° are respectively the vapour pressure of the compound considered

TABLE VI

	58°C		68°C		87°C		88°C	
	$a_{\text{calc.}}$	$a_{\text{exp.}}$	$a_{\text{calc.}}$	$a_{\text{exp.}}$	$a_{\text{calc.}}$	$a_{\text{exp.}}$	$a_{\text{calc.}}$	$a_{\text{exp.}}$
Methanol	1.29	1.34	1.25	1.32	1.22	1.27	1.20	1.24
Ethanol	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
1-Propanol	0.53	0.50	0.55	0.52	0.57	0.53	0.59	0.55
2-Propanol	1.02	1.03	1.05	1.07	1.06	1.07	1.07	1.08
1-Butanol	—	—	0.26	0.25	0.28	0.27	0.30	0.29
2-Butanol	—	—	0.58	0.58	0.61	0.59	0.63	0.61
2-Methyl-2-propanol	—	—	1.23	1.29	1.25	1.29	1.26	1.29
2-Methyl-2-butanol	—	—	0.62	0.63	0.64	0.65	0.66	0.67

and that of ethanol, γ_m and $\gamma_{m,E}$ being the corresponding activity coefficients. These data were compared with the experimental values:

$$\alpha_{\text{exp.}} = t_{r,E}/t_r$$

where t_r is the retention time of the sample and $t_{r,E}$ is the retention time of ethanol. The values listed in Table VI indicate a good agreement between theory and experiment. Since ΔH^E and $\Delta S_{\text{corr.}}$ are almost identical for all the alcohols studied, this behaviour is to be expected.

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